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Raman scattering evidence on the correlation of middle range order and structural self-organization of As-S-Ge glasses in the intermediate phase region

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Abstract

The Raman scattering of bulk nonstoichiometric chalcogenide alloys along the pseudo-binary AsS3 – GeS4 tie-line, which completely lies in the intermediate phase (IP) region of As-S-Ge ternary system was investigated in order to reveal the structural transformations in charge of the unusual features of the middle range order, elastic and physical-chemical parameters of these glasses observed earlier. It is shown that very narrow compositional areas can form inside the IP with high level of structural self-organization, mainly due to sudden increase of the concentration of highly flexible species such as quasi-tetrahedral (QT) S=As(S1/2)3 s.u. that comprises 4-fold coordinated As atoms. In the (GeS4)x(AsS3)1-x ternary system such a compositional area appears around the Ge7.7As15.3S77 (x =0.33; < r > = 2.31) composition that is a strongly self-organized glass with an assessed concentration of QT S=As(S1/2)3 around 30 % of total atomic clusters being the building blocks of the structure. This composition consists of minimal number of atomic building species, apart from QT S=As(S1/2)3 s.u. and free sulfur only the AsS3 pyramids and edge-sharing (ES) GeS4 tetrahedra have been revealed. Actually this self-organized state seems to be compositionally “metastable” as the variation of Ge concentrations by approximately transforms the most part of the QT S=As(S1/2)3 s.u. into either AsS3 pyramids or corner-sharing (CS) GeS4 tetrahedra, mixed with a number of others clusters of smaller concentration. A good correlation was found between the compositional dependence of Raman scattering normalized strengths and middle range ordering (MRO) parameters such as sizes of molecular domains (D) and correlated inter-domain distances (d), as well as the molar volume (Vm) and longitudinal elastic modulus (CL). MRO parameters and molar volume exhibit global minima around composition (As15,3 S77 Ge7,7; x = 0.33; < r > = 2.31) corresponding to strong self - organized glass

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that assign it as glass with most “packed” MRO structure and meanwhile the elastic modulus reaches its maximum value.

Keywords: chalcogenide glasses, Raman scattering, self-organized glasses

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